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Predictions of microwave and far-infrared transitions in $He–H_2^+$

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ABSTRACT

A new potential energy surface for the molecular ion $He–H_2^+$ is used to predict microwave transitions that may be observable in environments such as circumstellar envelopes and planetary nebulae. For the vibrational ground state, transitions are predicted at wavelengths of 1215, 608, 405, 304, 244, 203, 175, 154, 137 and 124 μm.

Key words: molecular processes – ISM: molecules.

1 INTRODUCTION

Chemical processes in the interstellar medium frequently involve molecular ions, especially in photodissociation regions such as circumstellar envelopes and planetary nebulae. Prominent species include CH^+, HCO^+ and N_2H^+. However, the simplest molecular ion, H_2^+, resists detection in the interstellar environment. Its lack of a dipole moment makes detection at infrared or radio frequencies difficult, although it does have a quadrupole spectrum that might be observable (Glinski, Schulz & Nuth 1997). However, the related ion $He–H_2^+$ may also be present, and it has a large dipole moment that might make detection feasible even at relatively low densities.

Bound $He–H_2^+$ cannot be produced in collisions between He and H_2^+ unless there is a third body present to remove the excess energy. This is unlikely in an interstellar environment, except perhaps in the inner regions of circumstellar envelopes. However, $He–H_2^+$ *can* be formed in collisions between metastable He and neutral H_2 by associative ionization,

$$He^* + H_2 \rightarrow HeH_2^+ + e^-. \quad (1)$$

It is thus worthwhile to investigate the signatures by which $He–H_2^+$ could be detected in interstellar space. To provide this information, rotation–vibration energy levels and microwave transitions calculated on a recently constructed potential energy surface (PES) are reported here.

2 CALCULATIONS

Until recently, most theoretical studies on $He–H_2^+$ used the potential energy surface calculated by McLaughlin & Thompson (1979, hereafter MT79) and subsequently fitted to a functional form by Joseph & Sathyamurthy (1987). For example, Tennyson & Miller (1987) used this early surface to calculate energy levels from which the microwave and infrared spectra of $He–H_2^+$ may be inferred. However, the MT79 surface is not very accurate, and Špirko & Kraemer (1995) and Falcetta & Siska (1996) have carried out improved calculations to remedy its more obvious deficiencies. Unfortunately, even these improved surfaces have not proved adequate to explain the recent spectroscopic studies of near-dissociation states of $He–H_2^+$ carried out by Carrington et al. (1996).

We have therefore calculated a new potential energy surface for $He–H_2^+$. The theoretical procedure is described in detail elsewhere (Meuwly & Hutson 1998). Interaction energies between He and H_2^+ were calculated using a quantum chemical approach with a very extensive basis set of atomic orbitals. The method chosen [QCISD(T)] incorporates most of the electron correlation contributing to the binding between He and H_2^+. The calculations are performed on a grid of 378 intermolecular configurations. In $He–H_2^+$ the three internal coordinates are the H_2^+ bond length r, the distance R from the helium atom to the centre of mass of H_2^+ and the angle θ between the two distance vectors. This Jacobi coordinate system is widely used in the study of intermolecular interactions.

In neutral complexes the coupling between internal degrees of freedom and the intermolecular coordinates R and θ is often very weak. Under these circumstances it is possible in a first approximation to fix r at the equilibrium separation of the monomer. This is not the case for $He–H_2^+$, so it was necessary to calculate the full three-dimensional potential energy surface.

The calculation of energy levels requires an analytical form for the potential surface. We fitted the energies to a flexible functional form which takes into account the correct R^{-4} long-range behaviour of the interaction (Meuwly & Hutson 1998). The fitted potential $V(R, r, \theta)$ was then used in the BOUND program (Hutson 1993) to calculate the rovibrational energies for the complete rotation–vibration Hamiltonian.

The states of H_2^+ and $He–H_2^+$ may be classified as either ortho or para for total nuclear spin quantum numbers $I = 1$ or 0 respectively. Ortho-H_2^+ can occupy only odd rotational levels while para-H_2^+ can occupy only even levels. The ortho/para symmetry is conserved in the complex (apart from very small terms arising from the nuclear hyperfine interaction). We find that the potential energy surface for $He–H_2^+$ supports 16 bound vibrational states of ortho symmetry and 14 states of para symmetry correlating with the $v = 0$ level of H_2^+. The infrared bending and intermolecular stretching fundamentals lie at 642 and 716 cm^{-1} respectively. The intramolecular stretch

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(H_2^+ $v = 1$) lies slightly above the dissociation limit of the complex at about 1825 cm^{-1}, redshifted by 370 cm^{-1} from the free H_2^+ monomer.

The potential energy surface for H_2^+ has pronounced minima at the two linear geometries, $\theta = 0^\circ$ and 180°. Because these two minima are equivalent and separated by a high barrier, the low-lying states of the complex occur as pairs separated by small tunnelling splittings. In the calculations, the even tunnelling levels arise solely from para states of H_2^+, and the odd levels arise from ortho states. The overall energy level pattern is essentially that of a linear molecule, except that each level occurs in ortho and para modifications, and the two have slightly different rotational constants. All the microwave lines of He–H_2^+ thus occur as closely spaced doublets. For the lower states, the splittings are too small to be resolved at current astronomical resolutions.

The principal aim of the present paper is to report on spectroscopic transitions predicted in the microwave and far-infrared region. The most promising microwave transitions for interstellar observation are the pure rotational transitions in the lowest few vibrational states. The rotational constant of He–H_2^+ is larger than those of most other species found in the interstellar medium. The lowest allowed ($J + 1 \leftarrow J$) rotational transitions for the ground state and the excited intermolecular stretching and bending state are given in Table 1. Further transition frequencies can be obtained from the authors upon request.

Table 1. Calculated rotational energy levels and line positions for the lowest few vibrational levels of He–H_2^+. The last line of each section gives the dipole moment of the vibrational state calculated for $J = 0$.

	Bound state energies (cm^{-1})		Allowed transitions (μm)		
J	ortho	para	$J' - J''$	ortho	para
Ground state					
0	−1754.269	−1754.251			
1	−1746.032	−1746.014	1–0	1214.05	1213.00
2	−1729.568	−1729.549	2–1	607.38	607.35
3	−1704.895	−1704.875	3–2	405.31	405.29
4	−1672.043	−1672.021	4–3	304.39	304.40
5	−1631.049	−1631.025	5–4	243.94	243.93
6	−1581.961	−1581.935	6–5	203.72	203.71
7	−1524.839	−1524.811	7–6	175.06	175.06
8	−1459.753	−1459.721	8–7	153.64	153.63
9	−1386.782	−1386.747	9–8	137.04	137.03
10	−1306.020	−1305.980	10–9	123.82	123.81
μ/ea_0	2.01	2.01			
Stretch					
0	−1038.379	−1038.412			
1	−1030.945	−1030.974	1–0	1345.10	1344.43
2	−1016.080	−1016.102	2–1	672.73	672.41
3	−993.791	−993.804	3–2	448.66	448.46
4	−964.088	−964.089	4–3	336.66	336.53
5	−926.976	−926.965	5–4	269.46	269.37
6	−882.460	−882.436	6–5	224.64	224.58
7	−830.534	−830.499	7–6	192.58	192.54
8	−771.182	−771.139	8–7	168.49	168.46
9	−704.379	−704.331	9–8	149.69	149.68
10	−630.101	−630.050	10–9	134.63	134.62
μ/ea_0	3.36	3.36			
Bend					
1	−1103.881	−1103.770			
2	−1087.459	−1087.349	2–1	608.95	608.99
3	−1062.860	−1062.751	3–2	406.52	406.54
4	−1030.123	−1030.017	4–3	305.47	305.49
5	−989.304	−989.200	5–4	244.98	244.00
6	−940.472	−940.369	6–5	204.78	204.79
7	−883.711	−883.609	7–6	176.18	176.18
8	−819.121	−819.020	8–7	154.82	154.83
9	−746.822	−746.721	9–8	138.31	138.31
10	−666.950	−666.849	10–9	125.20	125.20
μ/ea_0	3.09	3.09			

Error estimates for the reported transition wavelengths can be given using calculations on an interpolated potential energy surface. Although the functional form for the fit has been chosen carefully, the fit does not exactly reproduce all the energies calculated on the grid. We have therefore used the 'reproducing kernel' interpolation scheme (Ho & Rabitz 1996) to perform another set of bound-state calculations. The wavelengths of the transitions differ by no more than 1 μm from those reported in Table 1.

Since the production of $He–H_2^+$ in an astrophysical environment depends on metastable He, it will be most abundant in environments with a high photon flux (photodissociation regions). The most promising locations for its observation are thus circumstellar envelopes and planetary nebulae similar to those currently being searched for species such as HeH^+.

Finally, it may be noted that the dipole moments of HeH^+ and $He–H_2^+$ are similar in magnitude, so that the microwave detection limits for the two species are likely to be comparable. A straightforward estimate of the line strengths of the pure rotational lines can be obtained from the calculated dipole moments. The main contribution to the dipole moment of $He–H_2^+$ arises from the charge on H_2^+, which is located at a distance $\frac{2}{3}R$ from the centre of mass of the complex. The dipole moment of a specific vibrational state is thus given by $\frac{2}{3}e\langle R\rangle_v$, where the subscript indicates the vibrational state. Values of this quantity are included in Table 1.

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